Final Report on ONR/ARPA
Supported Grant on
"Composites with Improved Compressive Properties"
NO: N00014-91-J-1044
by
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INTRODUCTION

A two year program was initiated on October 1, 1990 to pursue new approaches on improving the compressive properties of polymer based composites. This included work directed at new kinds of reinforcing agents, improved matrices and on the fiber matrix interface. A number of significant breakthroughs were achieved as a result of this study. In the case of the polymer matrix studies sufficient progress was made to justify additional funding and time extensions throughJune 30, 1994 by ONR/ARPA to support developmental programs at Boeing, UTC and Alcoa.

KEY ACCOMPLISHMENTS

The key achievements of this program are discussed under the following headings.

A. Improved Resin Matrices
  1) Liquid Crystalline Polymers
  2) Cross-Linked Copolyesters.
B. New or Improved Reinforcing Agents
  1) Single Crystal Flakes of AlB_2
  2) Role of Microfibrillar Morphology
C. Fiber-Matrix Interface

A. Improved Resin Matrices

1. Liquid Crystalline Polymers

Using commercially available liquid crystalline copolyesters it was shown for the first time that these materials could be coated onto metal substrates (Steel, Al, Ti) to form tightly adherent coatings. The thin coatings (5-20 microns) provide outstanding corrosion and wear resistance for the metal substrate (an alternative to galvanization of steel). Also, two coated substrates will undergo solid state consolidation under heat and pressure to form a strong adhesive bond (typical lap shear properties ~ 1,800 psi). Alcoa and Boeing have confirmed these results in independent studies. Several problems were identified in attempts to pursue commercial development of these novel coatings. These included 1) relatively high cost of the

commercial LCP's 2) problems in coating metal surfaces because of the high polymer melt viscosity and 3) relatively modest interlaminar shear properties due to the presence of chain anisotropy. This work was published recently (1-3) and a program was then initiated to address these shortcomings (see next section)

2. Cross-linkable Aromatic Copolyesters

A cross-linkable aromatic copolyester was developed during this study which appears to solve the above indicated problems as well as providing important advantages for the design of high performance composites and structural foams.

Thus a mixture of two melt processible oligomers could be prepared from branched all aromatic copolyesters, where oligomer I was capped with carboxylic acid end groups and oligomer II with acetoxy groups. Such a mixture melted between 175°-225°C to a stable low viscosity melt. Heating at 250°-300°C led to rapid cross-linking of the structure with a total evolution of 6-7% by weight of acetic acid. Several different strategies were devised for processing these oligomers into useful articles and to minimize any deleterious effect of acetic acid evolution. Thus in the case of adhesives the metal substrate was easily coated with the low viscosity melt and the thin film could be cross-linked by heating from 250°-300°C. The cross-linked coating could then be further reacted in the solid state with another coating at 250°-300°C at pressures of several hundred psi, to form a strong adhesive bond (lap shear values of up to 2500 psi).

Even more striking results were observed in fabrication of carbon fiber composites. It was found that composites with less than 1% voids could be fabricated directly from the melt impregnated fibers. Presumably escape of the acetic acid (6-7%) was facilitated by several factors including the presence of the fiber matrix interface. With a relatively high cross-link density such composites were shown to retain 100% of their mechanicals at 200°C and 65% at 350°C. Furthermore continuous recycling from room temperature to 300°C over a period of 24 hours showed no deterioration in mechanical properties. To our knowledge there are no other polymer matrices known which display these features. This matrix appears to be the only known polymer which comes close to satisfying the stringent requirements for use of polymer composite in the high speed transport.

Structural foams were prepared by carrying out the crosslinking reactions at temperatures of 325°C where the rapid evolution of acetic acid acts to foam the cross-linked structure. The foams can range from tough and resilient to relatively brittle depending on the cross-link density. Typically, at 300°C the foam shows about a 10% compression set after an applied load for 12 hours. To our knowledge there are no commercially available structural

foams which are stable in air above 180°C. Hence, this system affords a number of potential advantages not only for high temperature structural applications but also for design of very low dielectric constant films for use in multi-chip module laminates. Both Boeing and UTRC have expressed considerable interest in these foams for a wide range of aircraft applications.

Other key features of these cross-linked polyesters include 1) potentially low cost of under $4.00/lb, 2) intrinsic flame resistance with an LOI ~ 0.40 and 3) capability to recycle the crosslinked polymer back to the starting oligomer. A number of companies have expressed interest in working with us to accelerate commercial development of this new class of polymer. A broad based patent application was submitted in early 1994. One preprint [4] has appeared as a result of this work.

B. New or Improved Reinforcing Agents

1. AlB_2 Flakes

In earlier work [5] by the PI single crystal flakes of AlB_2 had been shown to yield epoxy reinforced composites with very high compressive, flexural, and tensile properties. For example at volume loadings of 60% such composites displayed planar tensile, compressive, and flexural modulus values of 40-45 X 10^6 psi (typically graphite epoxy in a cross-plied orientation would yield values of only 7-12 X 10^6 psi). The strength on the other hand measured only 120 ksi primarily because of the presence of cubic AlB_{12} single crystals. The goal of the present program was to 1) define crystallization conditions from molten aluminum which would eliminate formation of AlB_{12}, 2) design a process which could use a commercially available AlB (5%) alloy which costs ~ $2.70/lb and 3) develop melt processing conditions of flakes in aluminum to go directly into finished articles at the desired flake concentrations.

At present the first two goals have been realized and good progress made on the third. Thus, it has been shown that the AlB_{12} can be eliminated by heating the aluminum melt to over 1350°C and then quenching to 900°C, the temperature at which AlB_2 crystallizes. Use of a low cost AlB (3%) alloy has been successfully demonstrated yielding 7% flakes in Al in the absence of AlB_{12}. Conditions for controlling the flake size and aspect ratio are also being defined. With respect to the 3rd goal techniques for filtering the Al melt have been defined yielding 15 to 20% by volume flakes. We are now looking for an industrial partner to accelerate work on fabrication of finished articles. Preliminary tests on composites containing 10-15% flakes indicate significantly improved compressive properties over SiC or Al_2O_3 particulate reinforced aluminum at the same concentration. If the mechanical properties at higher volume loadings of 50-60% are anywhere near the anticipated

values this program will represent the single most important breakthrough in the field of composites since the inception of this field. Thus for the first time low cost structural materials will be available which can be fabricated into finished articles directly from the melt andwhich display mechanical properties far higher than any known material. A patent application will be filed on this work shortly.

2. Role of Microfibrillar Morphology

The microfibrillar morphology present in most high strength/modulus fibers such as graphite, Aramid or polyethylene is usually looked upon as a structural flaw which partially contributes to the poor compressive properties of composites. To test this hypothesis we undertook to calender the Spectra fiber at elevated temperatures to reduce or eliminate these features. It was shown that Spectra fibers could be calendered at temperatures of 130°-140°C (m.p. 150°C) to produce a ribbon-like fiber (10/1 aspect ratio) where all of the shish-kebob morphology was eliminated and significant coalescence of the microfibrils was obtained. Although there was a major drop in the strength and modulus of the fiber, these values could be completely recovered by heat stretching 30-50% during calendering. Attempts to get Allied Signal to scale-up this work were unsuccessful, hence the results were recently published [(6)].

C. Fiber Matrix Interface

A technique for tailoring carbon fiber surfaces to optimize coupling to a specific resin matix was developed. Traditionally carbon fiber surfaces are oxidized to increase their interactions with a matrix such as an epoxy. In the present study high surface area carbon fibers where the pore surface had been chemically treated to yield highly acidic, basic or polar surfaces were used to measure the interactions between these surfaces and model organic molecules. The surfaces were prepared by treating the fiber with air, ammonia or chlorine at elevated temperatures to yield the desired surfaces. Adsorption isotherms were determined for typical small molecules such as ethers, alcohol, ketones, which were representative of the typical monomers present in the cross-linked matrix. It was shown that the various chemically treated surfaces displayed a selectivity toward the various small molecules suggesting that one could tailor the carbon fiber surface to be more selective toward specific matrix materials. This work was published [(7)] and not pursued further.

REFERENCES

1. J. Economy, T. Gogeva, V. Habbu, J. *Adhesion* 37, 215 (1992).

2. J. Economy and A. Andreopoulos, J. *Adhesion* 40, 115 (1993).

3. D. Frich, and J. Economy, *ACS PMSE Preprints* 69, 438 (1993).

4. J. Economy, D. Frich, K. Goranov and J. C. Lim, *ACS PMSE Preprints*, 70, 398 (1994).

5. L. Wohrer, A. Wosilait and J. Economy, *SAMPE*, 18, 340 (1993).

6. J. Economy, H. Jung and A. Andreopoulos, *Pol. for Adv. Tech.*, 3, 413 (1992).

7. J. Economy and A. Andreopoulos, *Pol. for Adv. Tech.*, in Press (1994).